

TITLELIGHT-EMITTING COPOLYMERS AND ELECTRONIC DEVICES
USING SUCH COPOLYMERSTHE INVENTION

5 The invention relates generally to pentaphenylene copolymers, and their use in electronic devices.

BACKGROUND INFORMATION

Organic electronic devices are present in many different kinds of electronic equipment. In such devices, an active layer is sandwiched
10 between two electrical contact layers. At least one of the electrical contact layers is light-transmitting so that light can pass through the electrical contact layer. One type of electronic device is an organic light emitting diode (OLED), which holds promise for display applications due to its high power conversion efficiency and low processing costs. Such displays are
15 especially promising for battery-powered, portable electronic devices, including cell-phones, personal digital assistants, handheld personal computers, and DVD players. These applications call for displays with high information content, full color, and fast video rate response time in addition to low power consumption.

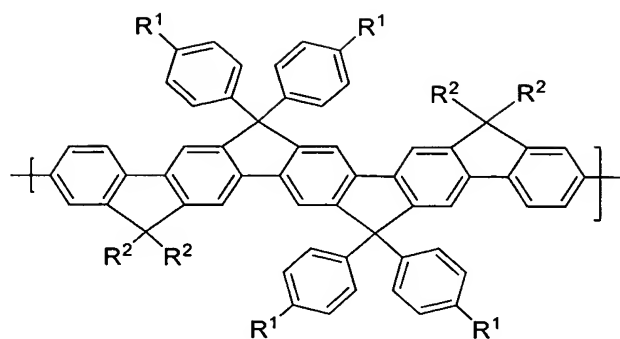
20 OLED's typically contain electroluminescent (EL) layers arranged between an anode and a cathode. Types of electroluminescent materials which have been used in OLED's include fluorescent dyes, fluorescent and phosphorescent metal complexes, conjugated polymers, and mixtures thereof. Several classes of luminescent polymers have also been
25 disclosed. These include, for example, poly(1,4-phenylene vinylene) and derivatives; polythiophenes, especially, poly(3-alkylthiophenes); and poly(p-phenylenes). Alkyl and dialkyl derivatives of polyfluorene have also been disclosed.

There is a continuing need for active compounds having the necessary
30 efficiency and color. In particular, blue-emitting polymers are desirable.

SUMMARY OF THE INVENTION

The invention provides a copolymer comprising a first monomeric unit having Formula I below:

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(I)

wherein:

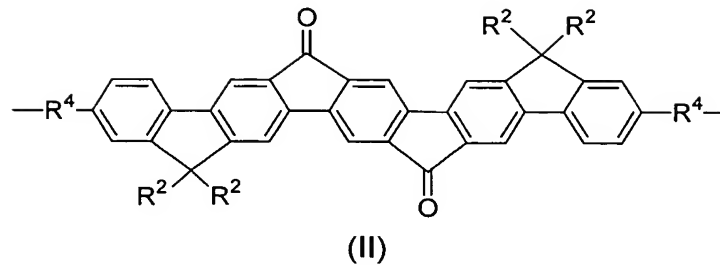
5 R^1 is the same or different at each occurrence and is selected from hydrogen, C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} alkoxy, C_1 - C_{20} oxyalkyl, C_2 - C_{20} oxyalkenyl, C_2 - C_{20} oxyalkynyl, C_1 - C_{20} fluorinated alkyl, C_2 - C_{20} fluorinated alkenyl, C_1 - C_{20} fluorinated oxyalkyl, C_2 - C_{20} fluorinated oxyalkenyl, C_2 - C_{20} fluorinated oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroaryl, -CN, -OR³, -CO₂R³,
10 -SR³, -N(R³)₂, -P(R³)₂, -SOR³, -SO₂R³, and -NO₂; or adjacent R groups together can form a 5- or 6-membered cycloalkyl, aryl, or heteroaryl ring,

15 R^2 is the same or different at each occurrence and is selected from C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} alkoxy, C_1 - C_{20} oxyalkyl, C_2 - C_{20} oxyalkenyl, C_2 - C_{20} oxyalkynyl, C_1 - C_{20} fluorinated alkyl, C_2 - C_{20} fluorinated alkenyl, C_1 - C_{20} fluorinated oxyalkyl, C_2 - C_{20} fluorinated oxyalkenyl, C_2 - C_{20} fluorinated oxyalkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, -CN, -OR³, -CO₂R³, -SR³, -
20 N(R³)₂, -P(R³)₂, -SOR³, -SO₂R³, and -NO₂; or adjacent R groups together can form a 5- or 6-membered cycloalkyl or heterocycloalkyl ring, and

25 R^3 is a substituent on a heteroatom which can be the same or different at each occurrence and is selected from hydrogen, alkyl, aryl, heteroalkyl and heteroaryl;

and at least one second monomeric unit comprising an aromatic group.

In one embodiment, the invention relates to a copolymer comprising the first monomeric unit and a second monomeric unit having Formula II
30 below:



5 wherein:

R^2 is as defined above, and

R^4 is the same or different at each occurrence and is selected from a single bond, alkylene, arylene, heteroalkylene, and heteroarylene.

10 In one embodiment, the invention relates to an electronic device having an active layer comprising at least one of the above copolymers.

As used herein, the term “aromatic group” is intended to mean an organic group comprising at least one unsaturated cyclic group having delocalized pi electrons. The term is intended to encompass both

15 aromatic hydrocarbon groups having only carbon and hydrogen atoms, and heteroaromatic groups wherein one or more of the carbon atoms within the cyclic group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like.

As used herein, the term “alkyl” refers to a monovalent straight or branched chain hydrocarbon group. The term “alkylene” refers to an alkyl group having two points of attachment.

20

As used herein, “alkoxy” refers to the moiety -O-alkyl-, wherein alkyl is as defined above.

As used herein, “oxyalkyl” refers to alkyl moieties in which at least

25 one -CH₂- unit of the alkyl moiety has been replaced by an oxygen atom.

As used herein, “alkenyl” refers to straight or branched chain hydrocarbonyl groups having one or more carbon-carbon double bonds.

As used herein, “oxyalkenyl” refers to alkenyl moieties in which at least one -CH₂- unit of the alkenyl moiety has been replaced by an oxygen atom.

30

As used herein, “alkynyl” refers to straight or branched chain hydrocarbonyl groups having one or more carbon-carbon triple bonds.

As used herein, "oxyalkynyl" refers to alkynyl moieties in which at least one -CH₂- unit of the alkenyl moiety has been replaced by an oxygen atom.

5 As used herein, "fluorinated" means that at least one hydrogen atom of the moiety has been replaced with a fluorine atom.

As used herein, the terms "heteroalkyl", "heteroalkenyl", and "heteroalkynyl" are intended to mean an alkyl group, an alkenyl group, and an alkynyl group, respectively, wherein one or more of the carbon atoms within the group has been replaced by another atom, such as nitrogen,
10 oxygen, sulfur, and the like.

As used herein, the term "aryl" is intended to mean a group derived from an aromatic hydrocarbon which may be unsubstituted or substituted. The term "arylene" refers to an aryl group having two points of attachment. The term "heteroaryl" is intended to mean an aryl group, wherein one or
15 more of the carbon atoms within the aryl group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like.

As used herein, the term "active material" is intended to mean a material which is electrically active or photoactive. Electrically active materials include conductive and semiconductive materials. The term
20 "photoactive" refers to any material that exhibits electroluminescence, photoluminescence, and/or photosensitivity.

As used herein, the term "blue," is intended to mean any color that appears bluish to the naked human eye, including light of wavelengths ranging from 400 nm to 540 nm.

25 As used herein, the term "emission maximum" is intended to mean the wavelength, in nanometers, at which the maximum intensity of electroluminescence is obtained. Electroluminescence is generally measured in a diode structure, in which the material to be tested is sandwiched between two electrical contact layers and a voltage is applied.
30 The light intensity and wavelength can be measured, for example, by a photodiode and a spectrograph, respectively.

As used herein, the term "monomeric unit" is intended to mean a repeating unit within a polymeric structure.

35 As used herein, the term "degree of polymerization" is intended to mean the total number of monomeric units in a polymer.

The IUPAC numbering system is used throughout, where the groups from the Periodic Table are numbered from left to right as 1-18 (CRC Handbook of Chemistry and Physics, 81st Edition, 2000).

As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, use of the "a" or "an" are employed to describe elements and components of the invention. This is done merely for convenience and to give a general sense of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In the formulae, all letters not otherwise defined, are used to designate conventional atomic symbols. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is illustrated by way of example and not limitation in the accompanying figures.

FIG. 1 includes an illustration of a cross-sectional view of an electronic device that includes a polymer in accordance with an embodiment of the present invention.

Skilled artisans appreciate that elements in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the elements in the figures

may be exaggerated relative to other elements to help to improve understanding of embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

5 The copolymer of the invention has a first monomeric unit having Formula I above which comprises a planar ladder-type pentaphenylene unit. This structure is intermediate between the monomeric units in fully ladder-type poly(p-phenylene) polymers ("LPPP") (reviewed by Scherf, *J. Mater. Chem.*, 1999, 9, 1853) and fluorene monomeric units (recent reviews are Neher, *Macromol. Rapid Commun.*, 2001, 22, 1365 and
10 Scherf and List, *Adv. Mater.*, 2002, 14, 477).

In the copolymers of the invention the rigidity of the first monomeric unit structure produces a small Stokes shift and high fluorescence efficiency. The aryl substituents improve the stability of the polymer against oxidation as previously shown in polyfluorenes (Müllen et al,
15 *JACS*, 2001, 123, 946; *Adv. Mater.*, 2002, 13, 809), while the avoidance of polymer analogous reaction steps avoids defects due to incomplete ring closure as is possible in LPPP.

The copolymers of the invention may exhibit blue electroluminescence. In one embodiment, the copolymer has an emission
20 maximum less than 450 nm.

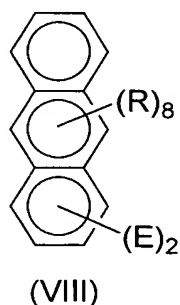
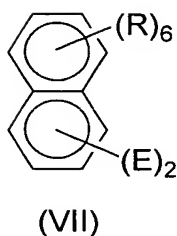
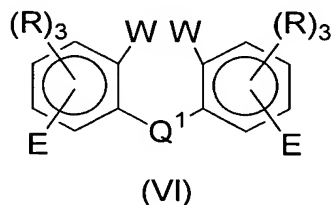
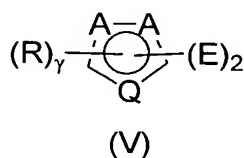
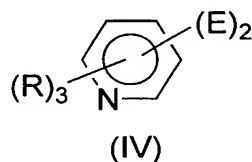
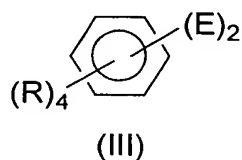
In one embodiment of Formula I, R¹ is selected from C₁₋₂₀ alkyls. In one embodiment, R¹ is selected from C₁₋₁₀ alkyls. In one embodiment all R¹ groups are the same. In one embodiment R² is selected from C₁₋₂₀ alkyls. In one embodiment R² is selected from C₁₋₁₀ alkyls. In one
25 embodiment all R² groups are the same.

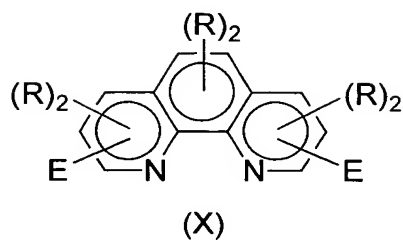
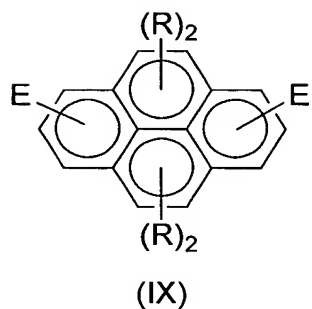
In the copolymers of the invention, there is at least one second monomeric unit comprising an aromatic group. Such monomeric units can be derived from mono- and polycyclic aromatic hydrocarbons and heteroaromatics. Examples of suitable aromatic groups include, but are
30 not limited to, fluorenes, spirofluorenes, phenyls, biphenyls, bridged biphenyls, naphthalenes, anthracenes, and the like, including mono- and poly-hetero analogs, and combinations thereof. The aromatic group can be substituted at one or more positions.

In one embodiment of the invention, the second monomeric unit
35 comprises Formula II. This monomeric unit has an electron accepting property. In one embodiment of Formula II, R⁴ is selected from a single bond and a phenylene. In one embodiment all R⁴ groups are the same. In one embodiment R² is selected from C₁₋₂₀ alkyls. In one embodiment R²

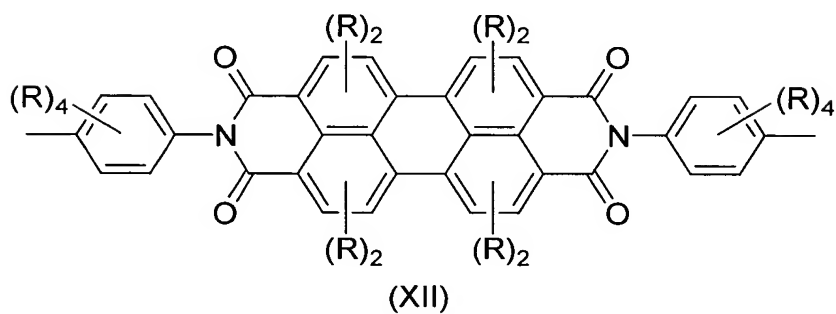
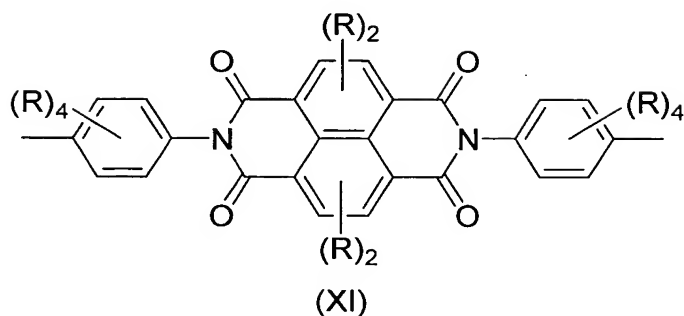
is selected from C₁₋₁₀ alkyls. In one embodiment all R² groups are the same.

In one embodiment of the invention, the at least one second monomeric unit is selected from (i) aromatic groups having Formula III below; (ii) 6-membered-ring heteroaromatic groups having Formula IV below; (iii) 5-membered-ring heteroaromatic groups having Formula V below; (iv) aromatic groups having Formula VI below; (v) fused ring aromatic groups having Formula VII through Formula XII below; and (vi) combinations thereof,





5



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where:

in each of Formulae III through XII:

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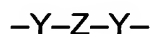
R is a substituent on a carbon atom which can be the same or different at each occurrence and is selected from hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkoxy, C₁-C₂₀ oxyalkyl, C₂-C₂₀ oxyalkenyl, C₂-C₂₀ oxyalkynyl, C₁-C₂₀

fluorinated alkyl, C₂-C₂₀ fluorinated alkenyl, C₁-C₂₀ fluorinated
 oxyalkyl, C₂-C₂₀ fluorinated oxyalkenyl, C₂-C₂₀ fluorinated
 oxyalkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl,
 heteroaryl, -CN, -OR³, -CO₂R³, -SR³, -N(R³)₂, -P(R³)₂, -SOR³,
 5 -SO₂R³, and -NO₂; or adjacent R groups together can form a 5-
 or 6-membered cycloalkyl, aryl, or heteroaryl ring;
 R³ is a substituent on a heteroatom which can be the same or
 different at each occurrence and is selected from hydrogen,
 alkyl, aryl, heteroalkyl and heteroaryl
 10 in each of Formulae III, IV, V, VI, VII, VIII, IX and X:
 E can be the same or different at each occurrence and is a single
 bond or a linking group selected from arylene and
 heteroarylene;
in Formula V:
 15 A is independently at each occurrence C or N and γ is 0 or an
 integer selected from 1 or 2, such that when both A are N, then γ
 is 0; or when one of A is N and one of A is C, then γ is 1; or
 when both A are C, then γ is 2;
 Q is O, S, SO₂, or NR³ where:
 20 R³ is a substituent on a heteroatom which can be the same or
 different at each occurrence and is selected from hydrogen,
 alkyl, aryl, heteroalkyl and heteroaryl;
in Formula VI:
 Q¹ is a carbonyl group, O, S, SO₂, or NR³ where:
 25 R³ is a substituent on a heteroatom which can be the same or
 different at each occurrence and is selected from hydrogen,
 alkyl, aryl, heteroalkyl and heteroaryl;
 W is H, alkyl or heteroalkyl; or both of W together can represent one
 single bond;
 30 in Formula VII:
 the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, or 2,6- positions;
in Formula VIII:
 the two E's are in the 1,4-, 1,5-, 1,8-, 2,3-, 2,6-, or 9,10- positions;
in Formula IX:
 35 a first E is in the 1, 2, or 3 position, a second E is in the 6, 7, or 8
 position; and

in Formula X:

a first E is in the 2, 3, or 4 position; a second E is in the 7, 8, or 9 position.

5 In one embodiment of the invention, the second monomeric unit comprises an electron deficient group ("ED unit") and has a formula



wherein:

10 Y is an aromatic group with at least one substituent selected from alkyl, heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and NR⁵,

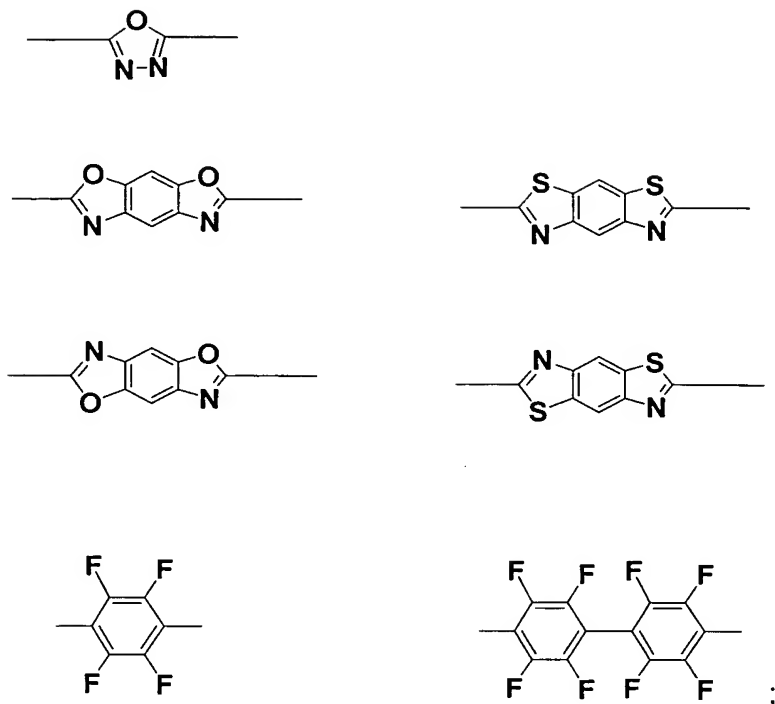
R⁵ is H or an alkyl; and

Z is an electron deficient group.

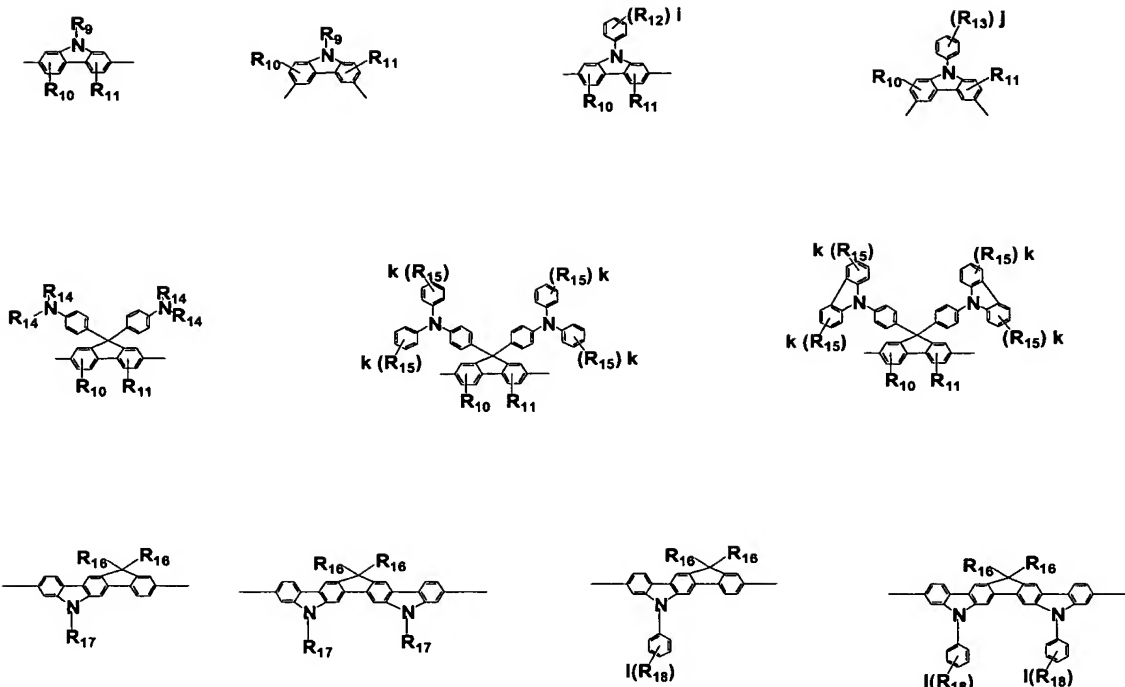
15 Examples of suitable aromatic groups for Y include mono- and polycyclic aromatic hydrocarbons, such as fluorenes, spirofluorenes, phenyls, biphenyls, bridged biphenyls, naphthalenes, anthracenes, and the like. The aromatic group can be substituted at one or more positions, preferably two positions. In one embodiment, the substituents are alkyl
20 groups having from 1 to 20 carbon atoms. In one embodiment the Y groups are fluorenes with two alkyl groups in the 9-position.

Examples of suitable electron deficient groups for Z include heteroaromatic groups having heteroatoms selected from O, N, and S, and fluorinated aromatic groups. In one embodiment, Z is selected from
25 oxazole-type, oxadiazole-type, thiazole-type, and fluorinated aromatic groups, such as phenyls and biphenyls.

In one embodiment, the Z group is selected from:



In one embodiment of the invention, the second monomeric unit is one having hole transport properties ("HT unit"). In general, the HT monomeric unit has an electron rich group. Examples of suitable HT monomeric units include, but are not limited to, carbazoles, triaryl amines, and aromatic groups having carbazole or triarylamine groups. Of particular interest as hole-transport monomers are the N-aryl carbazoles with alkyl substituents as they have better solubility and better processibility compared to other hole-transport monomers. Specific examples include:

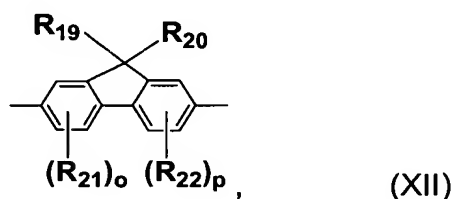


wherein:

R₉-R₁₈ are same or different and are selected from alkyl,
heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and NR⁵,
R⁵ is H or an alkyl;

i, j, k, l are numbers of substituents on the benzene rings and are
same or different and each of i, j, k, and l is in a range of 0-3.

In one embodiment of the invention, the second monomeric unit is
one which enhances the solubility of the resulting polymer ("SE unit").
Examples of suitable SE monomeric units include, but are not limited to,
substituted fluorenes, substituted phenyls, substituted biphenyls, and
substituted bridged biphenyls. In one embodiment, the SE monomeric unit
has Formula XII below:

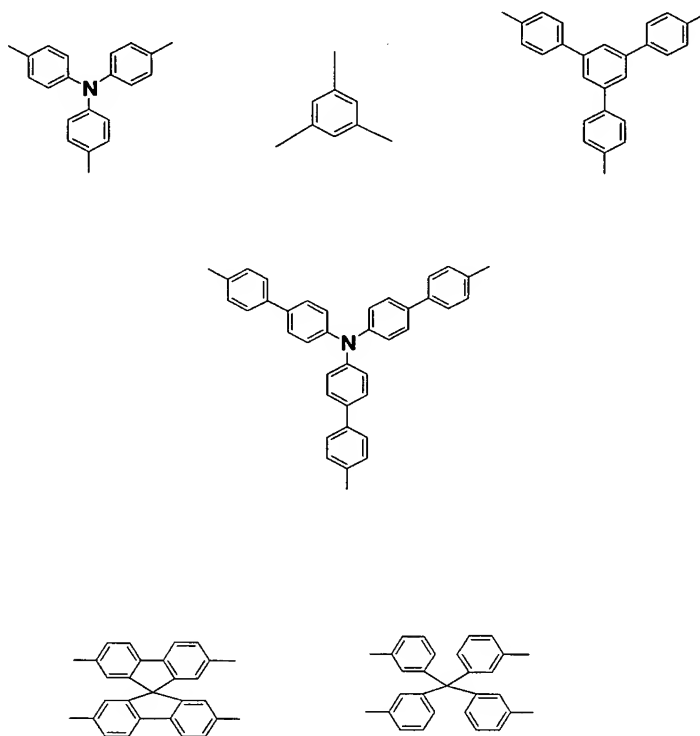


wherein

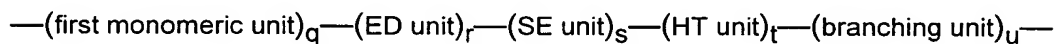
R₁₉-R₂₂ are same or different and are selected from alkyl,
heteroalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, and N R⁵,
R⁵ is H or an alkyl; and

o and p are numbers of substituents on the benzene rings and are same or different and each of o and p is in a range of 0-3.

In one embodiment of the invention, the second monomeric unit is a branching monomeric unit having more than two linkage sites. Examples of suitable branching monomeric units include, but are not limited to:



In the copolymer of the invention, more than one of the second monomeric unit can be present with the first monomeric unit. For example, the copolymer can have the formula



wherein:

the first monomeric unit has Formula I as described above;

the ED, SE, HT, and branching units are as defined above;

q is an integer; and

r, s, t, and u are 0 or an integer, with the proviso that at least one of

r, s, t, and u is an integer.

The relative molar proportion of first monomeric unit to the at least one second monomeric unit(s) can be from 99.9:0.1 to 1:99 or 99.5:0.5 to 10:90; alternatively 99:1 to 20:80, and further alternatively 99:1 to 50:50.

The incorporation of the monomers in the formation of the polymer can be random or controlled, resulting in copolymers which include, but are not limited to, random copolymers, alternating copolymers and block copolymers.

5 The copolymers of the invention, generally comprise at least 3 first monomeric units. In one embodiment, the copolymer comprises at least 10 first monomeric units. In one embodiment, the copolymer comprises at least 50 first monomeric units.

10 In the copolymers of the invention, the degree of polymerization is generally at least 5. In one embodiment, the degree of polymerization is at least 10. In one embodiment, the degree of polymerization is at least 50.

Synthesis

 The copolymers of the invention can generally be prepared by three known synthetic routes. In the first synthetic method, as described in
15 Yamamoto, *Progress in Polymer Science*, Vol. 17, p 1153 (1992), the dihalo derivatives of the monomeric units are reacted with a stoichiometric amount of a zerovalent nickel compound, such as bis(1,5-cyclooctadiene)nickel(0). In the second method, as described in Colon et al., *Journal of Polymer Science, Part A, Polymer chemistry Edition*, Vol.
20 28, p. 367 (1990). The dihalo derivatives of the monomeric units are reacted with catalytic amounts of Ni(II) compounds in the presence of stoichiometric amounts of a material capable of reducing the divalent nickel ion to zerovalent nickel. Suitable materials include zinc, magnesium, calcium and lithium. In the third synthetic method, as
25 described in US Patent 5,962,631, and published PCT application WO 00/53565, a dihalo derivative of one monomeric unit is reacted with a derivative of another monomeric unit having two reactive groups selected from boronic acid, boronic acid esters, and boranes, in the presence of a zerovalent palladium catalyst, such as tetrakis(triphenylphosphine)Pd.
30 The di-tosylate derivatives of the monomeric units can also be used.

 In some embodiments of the invention, the copolymer can be reacted with an end-capping compound to convert the reactive end group to a non-reactive end group. The end-capping compound is generally added to a preformed polymer and ends the polymerization reaction. The
35 end-capping compound is generally an aromatic compound having a single reactive group, such as an aromatic ring having a single halide group or boronic acid or ester group. Examples of suitable end-capping compounds include 9-bromoanthracene, 4-bromo-1,2-dimethoxybenzene,

1-bromopyrene, iodobenzene, bromobenzene, 2-bromo-9-fluorenone, and benzenboronic acid. The end-capping group may also be designed to add functionality, such as charge transport properties and color shifting. It may also affect interchain aggregation.

5 The copolymers of the invention can be used in electronic devices. FIG. 1 illustrates an exemplary electronic device 100 that includes an active layer positioned between two electrical contact layers. The electronic device 100 includes a hole transport layer 120 located between the active layer 130 and an anode layer 110. An optional electron
10 transport layer 140 is located between the active layer 130 and a cathode layer 150. Depending on the application of the device 100, the active layer 130 can be a light-emitting layer that is activated by an applied voltage (such as in a light-emitting diode or light-emitting electrochemical cell), a layer of material that responds to radiant energy and generates a
15 signal with or without an applied bias voltage (such as in a photodetector). Examples of photodetectors include photoconductive cells, photoresistors, photoswitches, phototransistors, phototubes, and photovoltaic cells, as described in Markus, John, *Electronics and Nucleonics Dictionary*, 470 and 476 (McGraw-Hill, Inc., 1966). The device is not limited with respect
20 to system, driving method, and utility mode. The polymers may be used as part of an organic active layer, hole-transport layer, or electron-transport layer in an organic light-emitting diode ("OLED") of a display. When used in OLEDs, some of the best device performances to date including high efficiency and blue color purity have been achieved.
25 The device may include a support or substrate (not shown) that can be adjacent to the anode layer 110 or the cathode layer 150. Most frequently, the support is adjacent the anode layer 110. The support can be flexible or rigid, organic or inorganic. Generally, glass or flexible organic films are used as a support. The anode layer 110 is an electrode
30 that is more efficient for injecting holes compared to the cathode layer 150. The anode can include materials containing a metal, mixed metal, alloy, metal oxide or mixed-metal oxide. Suitable metals include the Group 11 metals, the metals in Groups 4, 5, and 6, and the Group 8-10 transition metals. If the anode layer 110 is to be light transmitting, mixed-metal
35 oxides of Groups 12, 13 and 14 metals, such as indium-tin-oxide, may be used. Some non-limiting, specific examples of materials for anode layer 110 include indium-tin-oxide ("ITO"), aluminum-tin-oxide, gold, silver,

copper, nickel, and selenium. The anode may also comprise an organic material such as polyaniline.

The anode layer 110 may be formed by a chemical or physical vapor deposition process or spin-cast process. Chemical vapor deposition may be performed as a plasma-enhanced chemical vapor deposition ("PECVD") or metal organic chemical vapor deposition ("MOCVD"). Physical vapor deposition can include all forms of sputtering, including ion beam sputtering, as e-beam evaporation and resistance evaporation. Specific forms of physical vapor deposition include rf magnetron sputtering or inductively-coupled plasma physical vapor deposition ("IMP-PVD"). These deposition techniques are well known within the semiconductor fabrication arts.

Examples of materials which may facilitate hole-injection/transport comprise N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) and bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP); hole-transport polymers such as polyvinylcarbazole (PVK), (phenylmethyl)polysilane, poly(3,4-ethylenedioxythiophene) (PEDOT), and polyaniline (PANI), or the like; electron and hole-transporting materials such as 4,4'-N,N'-dicarbazole biphenyl (BCP); or light-emitting materials with good hole-transport properties such as chelated oxinoid compounds, including tris(8-hydroxyquinolato)aluminum (Alq₃) or the like. In some embodiments, if the conductivity of the hole-injection/transport layer 120 can be made similar to anode layer 110, the anode layer 110 may not be required and the hole-injection/transport layer 120 can act as the anode for the electronic device.

The hole-injection/transport layer 120 can be formed using any conventional means, including spin-coating, casting, and printing, such as gravure printing. The layer can also be applied by ink jet printing, thermal patterning, or chemical or physical vapor deposition.

Usually, the anode layer 110 and the hole-injection/transport layer 120 are patterned during the same lithographic operation. The pattern may vary as desired. The layers can be formed in a pattern by, for example, positioning a patterned mask or resist on the first flexible composite barrier structure prior to applying the first electrical contact layer material. Alternatively, the layers can be applied as an overall layer (also called blanket deposit) and subsequently patterned using, for example, a patterned resist layer and wet chemical or dry etching techniques. Other

processes for patterning that are well known in the art can also be used. When the electronic devices are located within an array, the anode layer 110 and hole-injection/transport layer 120 typically are formed into substantially parallel strips having lengths that extend in substantially the same direction.

The polymers of the invention have particular utility in the active layer 130. This layer can be applied from solutions by any conventional technique, including spin-coating, casting, and printing.

Optional layer 140 can function both to facilitate electron-injection/transport, and also serve as a buffer layer or confinement layer to prevent quenching reactions at layer interfaces. More specifically, layer 140 may promote electron mobility and reduce the likelihood of a quenching reaction if layers 130 and 150 would otherwise be in direct contact.

Examples of materials which may facilitate hole-injection/transport comprise metal-chelated oxinoid compounds (e.g., Alq₃ or the like); phenanthroline-based compounds (e.g., 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ("DDPA"), 4,7-diphenyl-1,10-phenanthroline ("DPA"), or the like); azole compounds (e.g., 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole ("PBD" or the like), 3-(4-biphenyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole ("TAZ" or the like); other similar compounds; or any one or more combinations thereof. Alternatively, optional layer 140 may be inorganic and comprise BaO, LiF, Li₂O, or the like.

The electron-injection/transport layer 140 can be formed using any conventional means, including spin-coating, casting, and printing. The layer can also be applied by ink jet printing, thermal patterning, or chemical or physical vapor deposition.

The cathode layer 150 is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode layer 150 can be any metal or nonmetal having a lower work function than the first electrical contact layer (in this case, the anode layer 110). Materials for the second electrical contact layer can be selected from alkali metals of Group 1 (e.g., Li, Na, K, Rb, Cs,), the Group 2 (alkaline earth) metals, the Group 12 metals, the rare earths, the lanthanides (e.g., Ce, Sm, Eu, or the like), and the actinides. Materials such as aluminum, indium, calcium, barium, yttrium, and magnesium, and combinations, may also be used. Specific non-limiting examples of materials for the cathode layer 150

include barium, lithium, cerium, cesium, europium, rubidium, yttrium, magnesium, and samarium.

5 The cathode layer 150 is usually formed by a chemical or physical vapor deposition process. In general, the cathode layer will be patterned, as discussed above in reference to the anode layer 110 and optional
10 conductive polymer layer 120. If the device lies within an array, the cathode layer 150 may be patterned into substantially parallel strips, where the lengths of the cathode layer strips extend in substantially the same direction and substantially perpendicular to the lengths of the anode
layer strips. Electronic elements called pixels are formed at the cross points (where an anode layer strip intersects a cathode layer strip when the array is seen from a plan or top view).

In other embodiments, additional layer(s) may be present within organic electronic devices. For example, a layer (not shown) between the
15 conductive polymer layer 120 and the active layer 130 may facilitate positive charge transport, band-gap matching of the layers, function as a protective layer, or the like. Similarly, additional layers (not shown) between the active layer 130 and the cathode layer 150 may facilitate negative charge transport, band-gap matching between the layers,
20 function as a protective layer, or the like. Layers that are known in the art can be used. In addition, any of the above-described layers can be made of two or more layers. Alternatively, some or all of inorganic anode layer 110, the conductive polymer layer 120, the active layer 130, and cathode
layer 150, may be surface treated to increase charge carrier transport
25 efficiency. The choice of materials for each of the component layers may be determined by balancing the goals of providing a device with high device efficiency with the cost of manufacturing, manufacturing complexities, or potentially other factors.

Although not meant to limit, the different layers may have the
30 following range of thicknesses: inorganic anode layer 110, usually no greater than approximately 500 nm, for example, approximately 10-200 nm; conductive polymer layer 120, usually no greater than approximately 250 nm, for example, approximately 20-200 nm; active layer 130, usually no greater than approximately 1000 nm, for example,
35 approximately 10-80 nm; optional layer 140, usually no greater than approximately 100 nm, for example, approximately 20-80 nm; and cathode layer 150, usually no greater than approximately 100 nm, for example, approximately 30-500 nm. If the anode layer 110 or the cathode layer 150

needs to transmit at least some light, the thickness of such layer may not exceed approximately 100 nm.

In polymer light emitting diodes, electrons and holes, injected from the cathode 150 and anode 110 layers, respectively into the active polymer layer 130, form negative and positively charged polarons in the polymer. These polarons migrate under the influence of the applied electric field, forming a polaron exciton with an oppositely charged species and subsequently undergoing radiative recombination. A sufficient potential difference between the anode and cathode, usually less than approximately 12 volts, and in many instances no greater than approximately 5 volts, may be applied to the device. The actual potential difference may depend on the use of the device in a larger electronic component. In many embodiments, the anode layer 110 is biased to a positive voltage and the cathode layer 150 is at substantially ground potential or zero volts during the operation of the electronic device. A battery or other power source(s) may be electrically connected to the electronic device as part of a circuit but is not illustrated in FIG. 1.

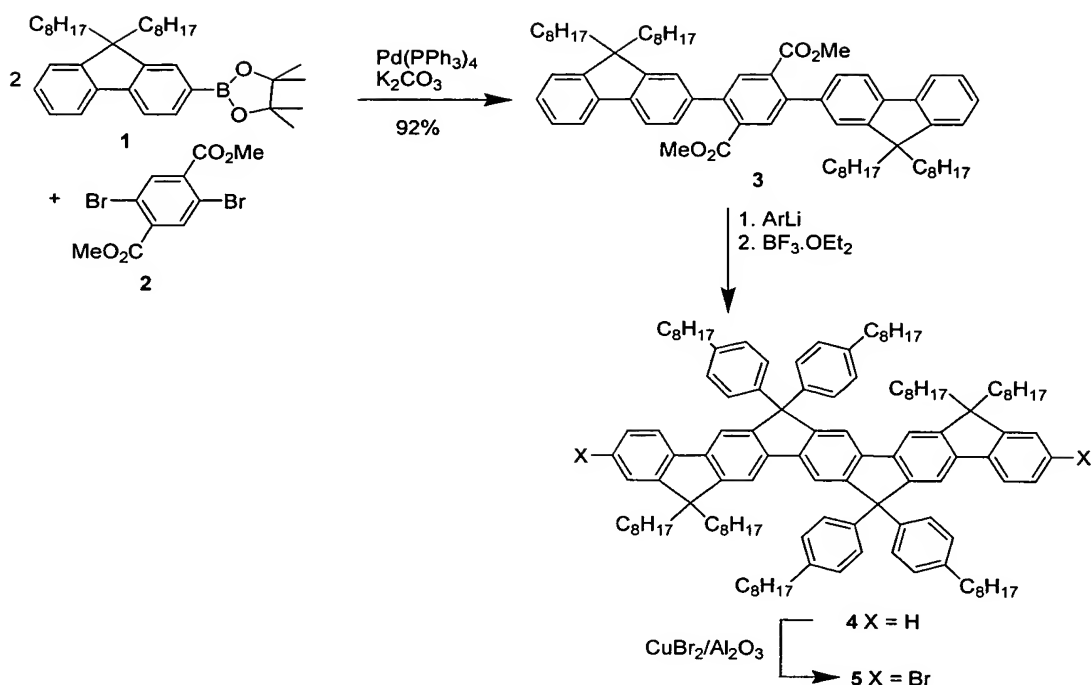
The invention will now be described in greater detail by reference to the following non-limiting examples.

EXAMPLES

Example 1

This example illustrates the preparation of a first monomer which can be used to prepare a copolymer of the invention..

As shown in the scheme below, Suzuki coupling of the fluorene-2-boronate ester **1**, with the dibromoterephthalate **2** generated an intermediate, the pentaphenylenediester **3** in 92 % yield. Addition of an excess of 4-alkylphenyl lithium produced a diol which was facilely ring-closed using BF_3 etherate to generate the ladder-type pentaphenylene **4** (95 %). Bromination of **4** using CuBr_2 on alumina²³ gave the monomer **5** (91 %).



Synthesis of the pentaphenylene diester **3**.

The boronate ester **1** (4.65 g, 9.0 mmol), diester **2** (1.52 g, 4.39 mmol), K_2CO_3 (1.21 g, 8.8 mmol) were dissolved in THF (40 mL) and water (20 mL) in a 100 mL schlenk flask. The solution was purged with argon for twenty minutes and then tetrakis(triphenylphosphine)palladium (152 mg, 0.03 equiv) was added and the reaction was heated with stirring at 85 °C. The reaction was followed by TLC and after 16 h was worked up. The cooled mixture was extracted with diethyl ether, and the extract was washed with saturated salt and then dried over MgSO_4 . The crude product so obtained was purified by chromatography on silica using 0-5 % ethylacetate in hexane as eluent. The product **3** was isolated as a thick viscous oil (3.94 g, 92 %). ^1H NMR: (CD_2Cl_2): δ 7.88 (s, 2H) 7.78 (m, 4H) 7.40-7.33 (m, 10H) 3.65 (s, 6H) 2.00 (t, 8H, $J = 8.5\text{ Hz}$) 1.21-1.07 (m, 40H) 0.62-0.83 (m, 20H) ppm. ^{13}C NMR: δ 169.26, 151.74, 151.62, 141.89, 141.56, 141.43, 139.54, 134.37, 132.44, 128.02, 127.82, 127.59, 123.84, 123.73, 120.55, 120.29, 55.96, 52.78, 41.16, 32.54, 30.81, 30.05, 29.99, 24.56, 23.35, 14.58 ppm. FDMS: m/z 971.3 Elemental Analysis: Calculated C 84.07 H 9.34 Found C 84.12 H 9.32.

Synthesis of the ladder-type pentaphenylene **4**.

- a) A solution of 4-octylbromobenzene (3.05 mL, 3.4 g, 12.6 mmol) in dry THF (40 mL) in a 250 mL schlenk flask, was cooled to -78 °C in an acetone/dry ice bath. n-Butyllithium in hexane (8.0 mL, 1.6 M, 12.8 mmol) was then added and stirred for 20 minutes. Then a solution of the diester **5** (2.05 g, 2.1 mmol) in dry THF (40 mL) was added dropwise with stirring and the solution was slowly allowed to warm to room temperature. The mixture was stirred overnight and then the quenched with brine. The mixture was extracted with diethyl ether, and the extract was washed with salt and dried over MgSO₄. The crude product was chromatographed on silica using 0-5 % ethylacetate in hexane as eluent to give the diol as a thick viscous oil. (3.39 g, 96 %). ¹H NMR: δ 7.61 (m, 2H) 7.45 (d, 2H, J = 7.6Hz) 7.29 (m, 6H) 7.12 (m, 16H) 6.76 (m, 4H) 6.69 (s, 2H) 3.11 (s, 2H) 2.61 (t, 8H, J = 7.6Hz) 1.77-0.45 (m, 128H) ppm. ¹³C NMR: δ 151.63, 151.23, 146.41, 144.19, 142.74, 141.71, 141.21, 141.05, 139.29, 136.29, 129.29, 128.76, 128.58, 127.93, 127.48, 124.32, 123.63, 120.35, 120.22, 83.91, 55.75, 40.55, 36.30, 32.72, 32.60, 32.45, 30.73, 30.30, 30.12, 30.09, 30.07, 30.04, 24.56, 23.46, 23.39, 14.65, 14.61 ppm. FDMS: m/z 1668.3.
- b) ring-closure: The diol (3.30 g, 1.98 mmol) was dissolved in dichloromethane (30 mL, used as purchased) and BF₃ etherate (0.20 mL) was added with stirring at room temperature. The colorless solution turned deep brown immediately upon addition and became light yellow within minutes. After 10 minutes, methanol (50 mL) was added to the solution whereupon the pentamer **4** started to precipitate as a colourless solid. The mixture was stirred for 12 h and then the solid was collected by filtration, washed with methanol and dried. The product was redissolved in dichloromethane and precipitated again by addition of methanol. Isolated yield of **4** = 3.06 g (95 %). ¹H NMR: δ 7.83 (s, 2H) 7.63 (m, 6H) 7.33-7.11 (m, 22H) 2.58 (t, 8H, J = 7.6Hz) 2.02 /t, 3H, J = 7.9Hz) 1.63-0.62 (m, 120H) ppm. ¹³C NMR: δ 152.80, 152.05, 151.88, 151.55, 144.35, 142.29, 141.83, 140.91, 140.87, 140.25, 129.11, 128.97, 127.63, 127.37, 123.65, 120.34, 118.16, 117.82, 115.35, 65.15, 55.61, 41.39, 36.28, 32.65, 32.55, 32.30, 30.82, 30.30, 30.22, 30.03, 30.01, 29.98, 24.67, 23.43, 23.34, 14.64, 14.60 ppm. FDMS: m/z 1633.2 . Elemental Analysis: Calculated C 89.75 H 10.25 %; Found: C 89.77 H 10.19 %.

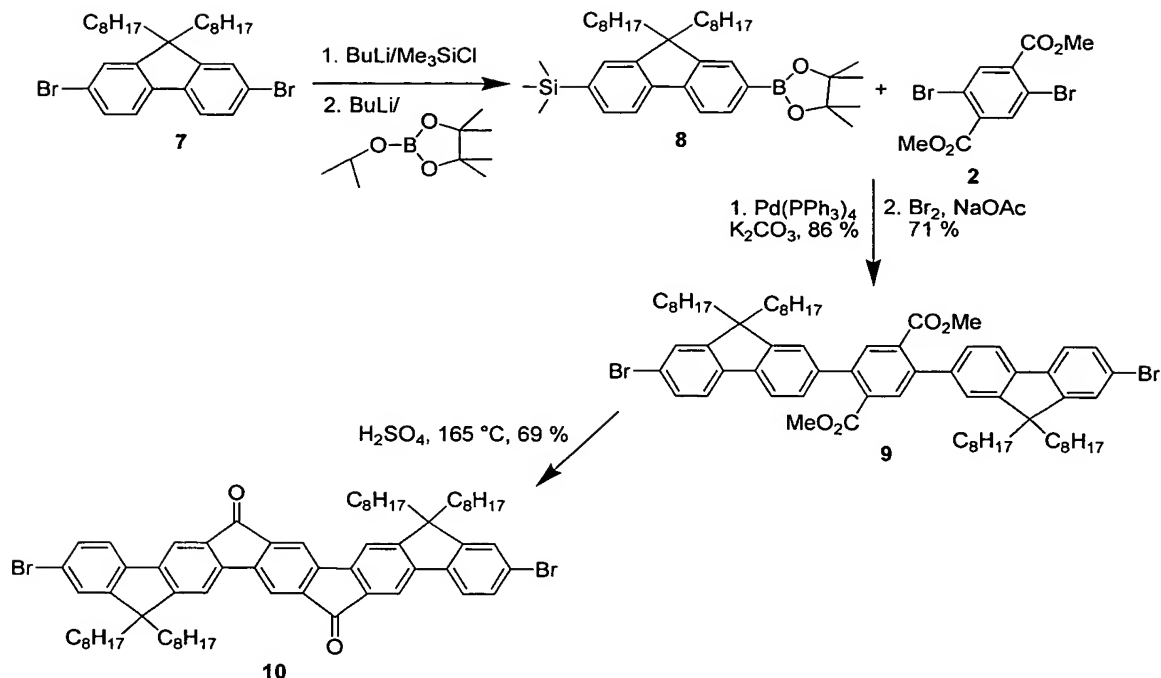
Synthesis of monomer 5.

The pentaphenylene **4** (0.80 g, 0.49 mmol) was added to carbon tetrachloride (30 mL) in a 100 mL round-bottomed flask, followed by CuBr₂ on alumina (2.0 g).²³ The reaction was heated under reflux with stirring and monitored by FDMS, which showed nearly quantitative formation of the dibromide after 14 h. The reaction mixture was concentrated, and the residue was loaded on silica and chromatographed on silica using hexane as eluent. The product **5** was isolated as a light yellow solid, (0.80 g, 91 %). ¹H NMR: δ 7.82 (s, 2H) 7.66 (d, 4H, J = 9.1Hz) 7.42 (m, 6H) 7.24 (d, 8H, J = 8.2Hz) 7.12 (d, 8H, J = 8.2Hz) 2.58 (t, 8H, J = 7.3Hz) 2.00 (t, 8H, J = 7.6Hz) 1.59 (m, 8H) 1.31-0.78 (m, 112H) ppm. ¹³C NMR: δ 154.19, 152.90, 152.30, 151.23, 144.17, 142.38, 140.97, 140.85, 140.76, 140.69, 130.52, 129.14, 128.95, 126.92, 121.79, 121.51, 118.29, 117.97, 115.44, 65.17, 55.99, 41.28, 36.26, 32.65, 32.53, 32.29, 30.73, 30.69, 30.29, 30.22, 30.00, 29.97, 24.62, 23.43, 23.35, 14.64, 14.60 ppm. FDMS: m/z 1780.50. Elemental Analysis: Calculated C 81.84 H 9.23 %; Found: 81.99 H 9.24 %.

Example 3

This example illustrates the preparation of a second monomer which can be used to form the copolymer of the invention.

As shown in the scheme below, 2,7-Dibromo-9,9-dioctylfluorene **7** was converted via the monosilyl compound to the boronate **8**. Suzuki coupling of this with the terephthalate **2** gave a crude disilylpentaphenylene in 86 % yield, which was converted to the dibromide **9** with sodium acetate and bromine (72 %). The monomers **5** could then be obtained by addition of aryllithium and ring closure, but in view of the longer synthesis and lower overall yield, this route is inferior to the previously described route. Treatment of **9** with concentrated sulphuric acid at 165 °C induced a double intramolecular Friedel-Crafts acylation to produce the desired diketone **10** in 65 % yield. By contrast treatment of the unbrominated diester **3** under the same condition gave incomplete ring closure.



Synthesis of 7-trimethylsilyl-9,9-di-n-octylfluorene-2-boronate 8.

- 5 n-Butyllithium in hexane (6.0 mL, 1.6 M, 9.6 mmol) was added to a solution of 2,7-dibromo-9,9-di-n-octylfluorene (**7**) (5.00 g, 9.13 mmol) in dry THF (50 mL) in a schlenk flask at -78 °C and the mixture was stirred for 20 minutes. Then chlorotrimethylsilane (1.5 mL, 1.29 g, 1.3 equiv) was added and the reaction was allowed to slowly warm to room temperature.
- 10 The mixture was stirred overnight and the reaction was quenched with saturated brine. The product was extracted into diethyl ether, and the extract was washed with brine and dried over MgSO₄. The crude product was chromatographed on silica using hexane as eluent to give 2-bromo-7-trimethylsilyl-9,9-di-n-octylfluorene as a colourless oil, (3.50 g, 71 %).
- 15 n-Butyllithium in hexane (4.4 mL, 1.6 M, mmol) was added to a solution of 2-bromo-7-trimethylsilyl-9,9-di-n-octylfluorene (3.47 g, 6.41 mmol) in dry THF (75 mL) in a schlenk flask at -78 °C, and the mixture was stirred for 20 minutes. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.44 mL, 1.31 g, 7.04 mmol) was added and the reaction was stirred for
- 20 24 h after warming to room temperature. The reaction was then quenched with brine, and the product was extracted into diethyl ether. The extract was washed with brine and dried over MgSO₄. The crude product was

chromatographed on silica using 0-3 % ethylacetate in hexane as eluent, to give **8** as a colourless solid (2.67 g, 71 %). ^1H NMR (CD_2Cl_2): δ 7.73 (m, 4H) 7.51 (m, 2H) 1.99 (t, 4H, $J = 8.2\text{Hz}$) 1.36-0.54 (m, 42H) 0.31 (s, 9H) ppm. ^{13}C NMR: δ 151.60, 151.34, 149.76, 145.29, 142.69, 141.07, 134.71, 133.01, 130.08, 129.03, 120.50, 120.25, 84.93, 56.22, 41.26, 33.01, 32.84, 31.11, 30.37, 25.98, 24.95, 23.85, 15.08, 0.01. FDMS m/z 588.90.

Synthesis of dibromopentaphenylene **9**.

The boronate ester **8** (2.45 g, 4.16 mmol), the diester **9** (697 mg, 1.98 mmol), and K_2CO_3 (821 mg) were dissolved in a mixture of THF (20 mL) and H_2O (10 mL) in a schlenk flask and the mixture was purged with argon for 20 minutes. To this tetrakis(triphenylphosphine)palladium (114 mg, 0.05 equiv) was added and the mixture was heated at 85°C for 20 h. The cooled mixture was extracted with diethyl ether, and the extract was washed with brine and dried over MgSO_4 . The residue was chromatographed on silica using 0-3 % ethylacetate in hexane to give the crude disilylpentaphenylene (1.89 g, 86 %).

In a schlenk flask, the diester **2** (1.89 g, 1.69 mmol) was added to dry THF (34 mL) along with anhydrous sodium acetate (278 mg, 2 equiv) and cooled to 0°C . Bromine (0.37 mL, 1.15 g, 4.2 equiv) was added and the mixture was stirred for 20 minutes. The reaction was quenched by addition of triethylamine (1.89 mL, 8 equiv) followed by an excess of aqueous Na_2SO_3 . The product was extracted into diethyl ether, and the extract was washed with sodium sulfite solution and dried over MgSO_4 . The residue was recrystallized from hot hexane to give the dibromide **9** as shiny colourless crystals (1.37 g, 72 %). ^1H NMR (CD_2Cl_2): δ 7.87 (s, 2H) 7.77 (d, 2H, $J = 7.9\text{Hz}$) 7.64 (d, 2H, $J = 7.9\text{Hz}$) 7.53-7.31 (m, 8H) 3.64 (s, 6H) 1.99 (t, 8H, $J = 8.8\text{Hz}$) 1.27-0.62 (m, 60H) ppm. ^{13}C NMR: δ 169.06, 154.06, 151.27, 141.89, 140.58, 140.49, 140.05, 134.32, 132.51, 130.76, 128.06, 127.04, 123.87, 122.01, 121.96, 120.46, 56.36, 52.82, 41.08, 32.54, 30.74, 30.03, 29.99, 24.52, 23.36, 14.59 ppm. FDMS m/z 1129.30 Elemental Analysis: Calculated C 72.33 H 7.85 %; Found C 72.75 H 7.91 %.

Synthesis of dibromopentaphenylenedione **10**.

The dibromide **9** (1.37 g) was added to 40 mL of 80 % H_2SO_4 (made from 4 mL H_2O and 36 mL conc. H_2SO_4) and heated with stirring at 165°C for 3h during which time the white solid turned brown. The acid was decanted off and the product was extracted into dichloromethane, and

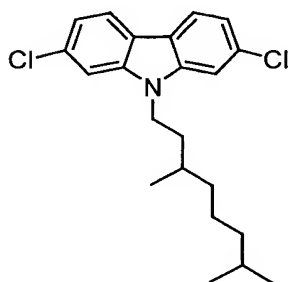
the extract was washed with sodium hydrogencarbonate solution and dried over MgSO_4 . The crude product was purified by chromatography on silica using 0-3 % ethylacetate in hexane as eluent to give the diketone **10** as a grey solid (0.88 g, 69 %). ^1H NMR (CD_2Cl_2): δ 7.97 (s, 2H) 7.86 (s, 2H) 7.65-7.49 (m, 8H) 2.03 (t, 8H, $J = 8.5\text{Hz}$) 1.25-0.62 (m, 60H) ppm. ^{13}C NMR: δ 192.91, 159.79, 153.77, 146.79, 144.19, 142.53, 140.81, 139.69, 134.70, 131.11, 127.10, 122.66, 122.21, 116.50, 116.38, 116.27, 56.96, 40.88, 32.53, 30.66, 29.97, 29.95, 24.60, 23.37, 14.60 ppm. Elemental Analysis: Calculated C 74.42 H 7.57 %; Found C 74.63 H 7.60 %.

Example 4

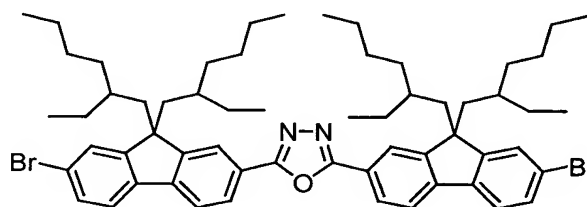
This example illustrates the preparation of a copolymer of the invention.

Comonomers:

Monomer **5** 40 mol%



20 mol%



40 mol%

Under inert conditions, DMF (7 mL) will be added to a Schlenk tube equipped with a stirring bar and containing *bis*(1,5-cyclooctadiene)nickel (0) (1.612 g, 5.86 mmol), 2,2'-bipyridyl (0.915 g, 5.86 mmol), and 1,5-cyclooctadiene (0.634 g, 5.86 mmol). The ensuing deep blue/purple solution will be stirred at 60 °C for 30 minutes, and then a solution of monomer **5** from Example 2 (2.065 g, 1.16 mmol), a second monomer, 2,5-bis-[7-bromo-9,9-bis-(2-ethyl-hexyl)-9H-fluoren-2-yl]-[1,3,4]oxadiazole (1.166 g, 1.16 mmol) a third monomer and 2,7-dichloro-9-(3,7-dimethyl-octyl)-9H-carbazole (0.218 g, 0.58 mmol) in toluene (28 mL) will be added via syringe. The reaction mixture will then be stirred at 75 °C for 24 h. The mixture will be cooled to room temperature and

precipitated into a solution of methanol (100 mL), acetone (100 mL) and concentrated hydrochloric acid (5 mL). After stirring for 2 hours, the mixture will be filtered. The solid residue will then be dissolved in chloroform, and again precipitated into a solution of methanol (100 mL), acetone (100 mL) and concentrated hydrochloric acid (5 mL). After stirring for 1 hour, the mixture will be filtered. The solid will again be dissolved in chloroform and precipitated in pure methanol. Finally the residue will be successively washed with methanol, water and methanol and dried in vacuo.

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